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Dr. Harin Ullal, Technical Monitor National Renewable Energy Laboratory 1617 Cole Boulevard Golden, CO 80401

Dear Harin,

This is the first quarterly report for Phase III for EPV's cost-shared subcontract RDJ-2-30630-21 **Advanced CIGS Photovoltaic Technology** awarded under the Thin Film Photovoltaics Partnership Program. The nominal period covered by the report is 12/1/03 - 2/29/04.

The core CIGS group consists of Dr. Alan Delahoy, Dr. Leon Chen, Dr. Baosheng Sang, Dr. Masud Akhtar, John Cambridge, Frank Ziobro, Ramesh Govindarajan, Renata Saramak and Siân Kleindienst. Ms. Kleindienst has a bachelors degree in physics from Harvard and joined EPV in November 2003. She expects to start graduate school at MIT in September 2004. Until then, she is carrying out CIGS module diagnostics.

This report summarizes the main activities conducted in this quarter. Almost all of the activities were associated with the production of large area CIGS modules in the pilot line, and their analysis.

- 1) Installation of full size dipping tanks for CBD CdS.
- 2) Investigation and solution of contact resistance problems.
- 3) Improvement of ZnO properties.
- 4) Development of all face-up patterning.
- 5) Large area module performance and analysis.
- 6) Extrinsic supply of sodium.
- 7) Plans for next quarter.
- 8) Other news.

1) Installation of full size dipping tanks for CBD CdS

We reported in our Phase II annual report that, with the exception of a full size CBD process, we restored EPV's large area CIGS module process in the last quarter of Phase II. As an interim step, 1 square foot modules were made, with all of the other steps being conducted on full scale equipment.

We were eventually able to finish installation of new large area dipping tanks for full size CBD CdS processing in the middle of this quarter. The chemical bath is contained in a stainless steel tank of dimension 42.5" x 22" x 2.5". The tank is fitted with a Chromalox Model 2110

temperature controller to monitor bath temperature. The heaters are attached lengthwise outside the tank in an insulated compartment. The chemical solution is agitated by a Masterflex B/T liquid pump Model 7585-12 and it is driven with a digital module to control solution flow in the range of 0.3 to 45 LPM. The tank is easy to maintain and to clean up. The process area is well vented to maintain safe operation.

The CdS films are deposited over two full size CIGS plates (38" x 17.5") which are clamped back-to-back and placed vertically in the center of the tank. CBD CdS is processed with moderate flow rate at low temperature at a slow deposition rate to yield uniform films. The deposition process is monitored by co-depositing two small pieces of CTO in the tank. The transmission of these CTO pieces at wavelengths of 420 nm and 440 nm is measured after deposition as an indication of film thickness. Sometimes the uniformity of the entire CdS film is checked. Listed in Table Ia and Ib is a typical distribution of transmission.

Table Ia. Transmission distribution of CTO deposited with CdS film at 420 nm

Width\Length	3"	11"	19"	27"	35"
3"	0.50	0.50	0.50	0.45	0.45
9"	0.50	0.50	0.50	0.43	0.50
15"	0.46	0.50	0.49	0.45	0.45

Table Ib. Transmission distribution of CTO deposited with CdS film at 440 nm

Width\Length	3"	11"	19"	27"	35"
3"	0.53	0.52	0.51	0.48	0.49
9"	0.53	0.54	0.51	0.48	0.54
15"	0.51	0.51	0.51	0.48	0.48

The device performance with CdS deposited in the large tank was compared with that obtained from small beaker CdS, which is our reference method. In Table II, the comparison results are compiled.

Table II. Comparison of device performance with CdS from the large tank and the beaker

Sample ID	Container	Position	Voc	FF	J_{sc}	Efficiency
			(mV)		(mA/cm^2)	(%)
Z1629-5D	Big Tank	Right bottom	539	70.5	30.2	11.5
Z1629-4B	Big Tank	Left bottom	545	67.1	30.1	11.0
Z1629-1C	Big Tank	Center	524	67.3	31.2	11.0
Z1629-3A	Big Tank	Right top	502	61.4	31.6	9.76
Z1629-1	Beaker		479	60.9	30.3	8.82
Z1629-2	Beaker		500	65.8	30.6	10.1

The results clearly show that the device performance with CdS from the big tank is at least as good as our reference CdS from the beaker.

2) Investigation and solution of contact resistance problems

In our large area module production, we often used to cut a small portion out of a full size CIGS plate and then process it into a 2" x 4" mini-module using manual patterning and/or ZnO deposited in the R&D Airco system as a process cross-check. For a period, we found that mini-modules deposited with Airco ZnO showed normal IV curves while those made with ZnO from the ILS (in-line system) exhibited a large series resistance. What puzzled us was that the ZnO co-deposited on plain glass in both systems, Airco and ILS, showed almost the same low value of sheet resistance. After extensive study and careful measurement, we finally established that the resistances of the ZnO on each cell (on CdS) were almost the same in both cases, but the contact resistance between the ZnO and Mo on the mini-modules was totally different from the two systems. ZnO deposited in the ILS yielded a much larger contact resistance than that from the Airco.

This led us to thoroughly investigate the issues related to contact resistance. In principle, high contact resistance could be caused by:

- Improper CIGS scratch
- Contaminated Mo surface
- Improper ZnO

At the beginning, much attention was paid to the first two causes since we assumed that low sheet resistance ZnO could not present a problem. We adjusted the CIGS mechanical scribing speed and pressure to make sure the CIGS layer was totally removed and the Mo exposed; we tried different scribing tips of various hardness to realize proper cutting profile such as flat bottom and no lift off; we increased the CIGS scribe width to increase the contact area; we tested ultrasonic cleaning of the substrate to replace the normal Bilco washer; we annealed CIGS after CdS to evaporate any water to prevent contamination in forming the contact. After extensive experimentation, none of these effects was found to be the root cause we were searching for although several of the variables were found to affect contact resistance.

Finally, we realized our low sheet resistance ZnO deposited in ILS was good for reduced ohmic loss as a front window layer while it performed badly as a contact. This was verified in the following experiment.

Fifteen 2" x 4" mini-modules were cut from the same CIGS plate Z1636. Two variables, n-ZnO deposition conditions and annealing after CdS, were chosen in this large experiment. The response variables, or the outcome variables, are median value of ZnO sheet resistance $R_{\rm sh}$ on the segments (15-16 segments per mini-module) and median value of contact resistance $R_{\rm con}$ between ZnO and Mo in each mini-module. The purpose of this experiment was to find out which condition would yield the lowest $R_{\rm sh}$ and $R_{\rm con}$. Listed in Table III are the experimental conditions and the results.

Table III. Experiment for sheet resistance R_{sh} and contact resistance R_{con}

ID	Anneal	System	ZnO conditions	Purpose	R _{sh}	R _{con}
110	111110	System	Ziro conditions	1 ui posc		
					(med)	(med)
					Ohm/sq	Ohm-cm
Z1636 1-1	No	ILS	Normal Process with Al carrier	Reference	23.1	4.35
Z1636 2-1	No	ILS	2. Normal Process with glass carrier	Carrier effects	25.1	7.67
Z1636 3-1	No	ILS	3.	Effect of	17.3	0.06
Z1636 4-1	No	ILS	4.	Effect of	27.2	0.16
Z1636 5-1	No	Airco	5. Power with RF and no O ₂	Different system	30.7	0.07
Z1636 1-1A	Yes	ILS	1	See above	29.1	3.10
Z1636 3-1A	Yes	ILS	3	See above	18.2	0.06
Z1636 4-1A	Yes	ILS	4	See above	39.4	0.20
Z1636 5-1A	Yes	Airco	5	See above	31.0	0.09
Z1636 1-2	No	ILS	1	See above	41.8	7.07
Z1636 3-2	No	ILS	3	See above	35.3	0.06
Z1636 4-2	No	ILS	4	See above	38.1	0.60
Z1636 1-2A	Yes	ILS	1	See above	22.8	6.05
Z1636 3-2A	Yes	ILS	3	See above	17.2	0.08
Z1636 4-2A	Yes	ILS	4	See above	24.3	0.70

Some of the conclusions drawn from these results are:

- Our original reference (Condition 1) does have a serious contact problem.
- Airco ZnO (Condition 5) works very well for a contact.
- Condition 4 improves R_{con} in an obvious way.
- The most significant improvement is from Condition 3
- Annealing after CdS deposition and glass carrier (Condition 2) do not affect R_{sh} and R_{con} much. It implies that water vapor is unlikely to be the usual contamination source.

Both in the PV industry and in publications people often use the sheet resistance R_{sh} of a ZnO layer as the sole parameter to judge n-ZnO electrical properties, which we have shown is an over-simplification for module production. As a result of this study, our contact problem was identified and solved.

In a further study of contact resistance, we found that a very poor contact between ZnO and Mo has a diode-like behavior, which is shown in Fig. 1 below. This experiment was conducted by passing forward current through the mini-module and directly measuring the voltage between the Mo and the ZnO over the Mo at the P₂ scribe position.

Z1625-2: IV curve on 5 different scribes

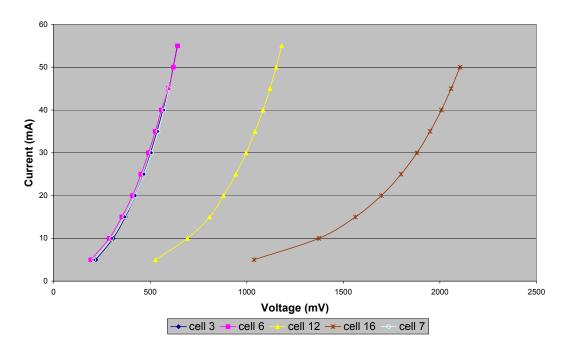


Fig. 1. I-V curves for exceptionally poor ZnO-Mo contacts

3) Improvement of ZnO properties

It was established that there is a huge properties gap of ZnO deposited in Airco (R&D system) and ILS (the pilot line system). Films deposited in the Airco are superior to those from the ILS. The data in Table IV and the plot in Fig. 2 show the difference.

Table IV. Electrical properties of n-ZnO deposited in Airco and ILS

System	Power Supply	Sheet R (Ohm/sq)	Thickness (Å)	Resistivity Ohm-cm
Airco	RF	8	7750	6.20E-04
ILS	Pulsed DC	12	15000	1.80E-03
ILS	RF	12	9580	1.15E-03

Comparison of AIRCO and DC&RF ILS n-ZnO

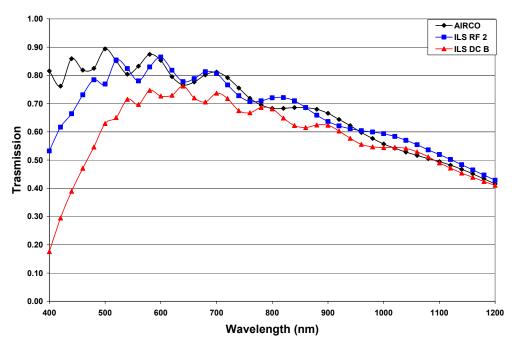


Fig.2. Optical transmission of n-ZnO films prepared by different methods

As we reported previously, n-ZnO deposited in the ILS turns out very dark in a pure Ar environment and therefore addition of a certain amount of O_2 is needed to improve the optical transmission. As a result, we have to double the thickness to maintain an acceptable sheet resistance because the resistivity increases significantly. And because of optical absorption we have to live with a large current loss to prevent substantial deterioration of FF.

As a comparison, listed in Table V are the main differences in hardware and operation between the two systems.

Table V. The hardware difference of Airco and ILS

System	Power Supply	Grounding	Spacing	Gas for n-ZnO	Deposition mode
Airco	RF	Substrate sits on	2.5 cm	Pure Ar	Static
		grounded metal			
ILS	Pulsed DC	Substrate	1.9 cm	Ar plus O ₂	Moving
		floating		•	

We carried out an extensive investigation using pulsed DC power supply in the ILS in this quarter. The variables included change of O_2 level, sputtering pressure, power, plate speed, pulse frequency, and pulse width. However, it appears that the n-ZnO was already optimized since no improvement could be realized.

We then decided to install a RF power supply and matching network in the ILS and, after careful grounding and shielding, the system was operated successfully. The resistivity of n-

ZnO improved substantially after that, and so did its optical properties (see Table IV and Fig. 2 above). Other factors, such as the effect of grounding and spacing, will be tested in the next quarter. Even so, two puzzles remain to be solved: we still need to add O_2 to the Ar environment to avoid film darkening, and films deposited in static mode still turn dark.

4) Development of all face-up patterning

A microscope with video image was installed on our full size X-Y table in this period. Although the real time inspected area is displaced from the actual scribing position, it nevertheless boosts our productivity greatly. Using the microscope we observed that the spacing between the CIGS scribe (P2) and the ZnO scribe (P3) is maintained constant while the spacing between P2 and P1 (the Mo scribe) is strongly variable and sometimes exhibits multiple crossovers. This results in an unacceptably large dead area in module production. In light of the fact that the plate is placed film side down for Mo scribing and film side up for CIGS and ZnO scribing we are convinced the non-parallel behavior is caused by the x-y table moving in a line that is not perfectly straight. Without major hardware changes, the only way to solve this problem is to develop a film-side-up Mo scribing operation at EPV, which is indeed being investigated. In section 5 we will report on the first module that was successfully fabricated this way.

Various mechanical scribing tips and blades were tested for CIGS and ZnO patterning, and we found eventually we have to compromise between the hardness of the tip (for longevity) and the smoothness of the scribed line.

Two other patterning projects, laser CIGS scribe and use of Cu_xSe as an inter-connection, were also briefly tested during this quarter, and further experiments are planned for the next quarter.

5) Large area module performance and analysis

We re-started our full size module production in this quarter following installation of full size CdS dipping tanks. Thirteen full size CIGS plates were attempted so far (to Z1655). Among these, two plates were broken during CIGS processing in the deposition system due to thermal stresses, and one broke unevenly during cutting. The first two modules made at the end of 2003 gave very low V_{oc} due to scribing crossover. They also had poor interconnects. The interconnect problem has now been solved. The performance of the remaining eight modules is listed in Table VI. (Runs 1647-1649 represented tests and experiments, not module production.) A new procedure for n-ZnO deposition was introduced starting with run Z1650, Z1653 had an older interconnect concept, and a more resistive i-ZnO was introduced with Z1655.

Module Z1652 after lamination yielded over 20W power with an efficiency 6.1% in an aperture area of 3355 cm². Its IV curve is plotted in Fig. 3. The last module for this quarter Z1655 showed the best performance with a power (measured outdoors very close to one sun and normalized to one sun) of 23.9W. The fill factor of 53.1% represents progress over previously mediocre fill factors. The aperture area efficiency is 6.7%.

Table VI. Performance of large area modules

ID	Voc	I _{sc} *	FF	Power	Efficiency	Segment	Voc/cell	Low-	Ap.
	(V)	(A)	(%)	(W)	(%)	#	(mV)	light	area
								Voc	(cm ²)
Z1643	26.1	0.978	52.3 [†]	13.3	5.6	50	522	9.9	2400
Z1644	28.5	0.91	46.6^{\dagger}	12.1	4.1	56	509	9.5	2980
Z1645	26.0	broken	during c	utting for m	neasurement	50	520	-	2500
Z1646	39.2	0.90	48.5 [†]	17.1	4.6	71	552	12.2	3700
Z1650	37.7	0.95	48.9	17.5	5.2	71	531	15.6	3354
Z1651	plate b	roken dur	ing first	IGS deposi	tion				
Z1652	40.3	1.01	50.6	20.5	6.1	71	567	16.6	3355
Z1653	37.1	1.09	44.0	17.8	5.0	71	522	7.0	3537
Z1653 ^{††}	31.1	0.203	51.2	3.2	6.9	55	564	13.1	470
Z1654**	37.6	1.08	49.3	20.0	5.4	71	530	7.7	3700
Z1655	39.5	1.05	53.1	23.9	6.7	71	559	19.2	3550

Measurements taken after light soaking for 15 hours.

^{††} Piece cut from plate

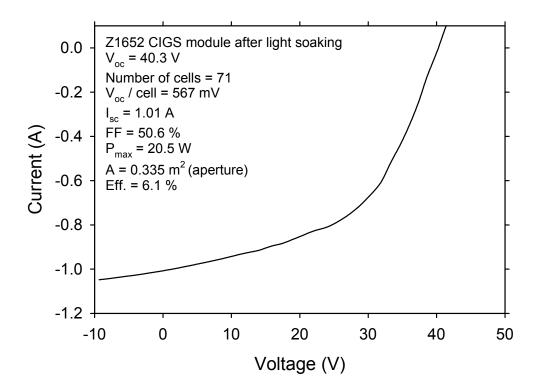


Fig. 3. I-V curve of laminated module Z1652 (6.1%, 20.5W)

^{*} Outdoor measurement normalized to one sun

[†] Corrected for bus bar loss

^{**} Lasered Mo side up; hot spots removed by hand

An average V_{oc} per cell of over 500 mV was achieved in all modules, with a best value of 567 mV in Z1652. The V_{oc} distribution for one module is shown in Fig. 4.

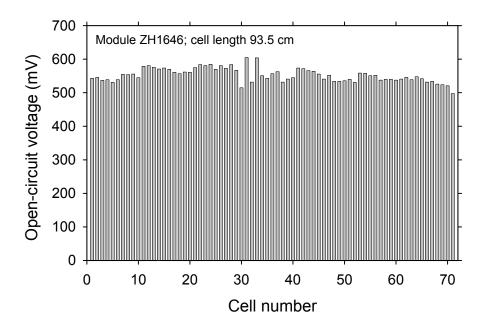


Fig. 4. Histogram of V_{oc} values for all cells of large module Z1646.

The low light V_{oc} (overall module figures shown in Table VI) was measured in fluorescent room light of approximately 0.0025 suns and is a further measure of module quality. Distributions are less uniform than the one-sun V_{oc} .

A reasonable FF was attained after implementation of new procedures leading to excellent contact resistances less than 0.1 ohm-cm. During this period, ZnO sheet resistances (on the CdS) were in the range 12-20 ohms/square. These numbers are acceptable, but could stand even further reduction to raise fill factor. Further improvement of FF requires improved CIGS quality and uniformity.

As an example of plate non-uniformity, we show in Table VI above measurement of a 470 cm² plate judiciously cut from the original 3540 cm² plate of run Z1653. The original plate was 5.0% while the best piece cut from it was 6.9%. Improvement of CIGS uniformity is now a top priority.

One of the root causes of non-uniformity is a fall off in the indium supplied to the long edges of the plate from the In linear source. In practice this causes many problems, including the need to add more In and Ga than is desirable in the third stage to prevent the edges remaining Cu rich at the end of the process. This distortion of the ideal recipe leads to a less than ideal spectral response. This is illustrated in Fig. 5. The limited red response is one reason why the modules suffer in current density.

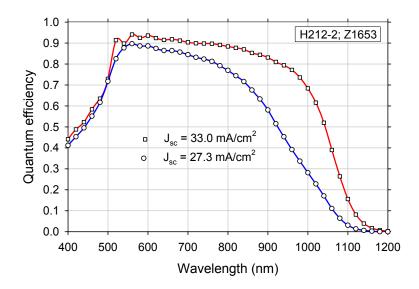


Fig. 5. Comparison of QE curves for a good R&D cell and a typical pilot line cell (Z1653).

EPV's overall progress to date with the hybrid process is shown in Fig. 6. This illustration was first presented in the Phase II annual report, and has been updated with the module and full-size module results obtained in this quarter.

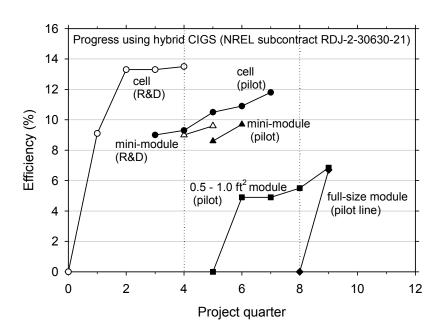


Fig. 6. Trajectory of progress with hybrid CIGS during the course of this subcontract.

In concluding this section we would like to comment that the production of well-performing CIGS modules is no longer a hit or miss affair, but that hard work has established the more user-friendly hybrid process, and has identified and solved several hidden problems, resulting in a reliable set of module production sub-processes that can now be optimized.

6) Extrinsic supply of sodium

The evaporation of NaF onto the Mo prior to CIGS deposition was performed in three increasingly careful and controlled experiments in the R&D system. In all three experiments a null result was obtained, i.e. cells with additional Na performed equally well on average as cells without additional Na. It was just staggering that we could not observe any difference. We have tentatively concluded that our Mo and hybrid CIGS processing already introduces sufficient Na (from the glass) into the film. Assuming this conclusion is correct, this is nevertheless useful information. For now, the topic of Na will be dropped.

7) Plans for next quarter (Q2)

The major focus will be on uniformity of CIGS composition and CIGS quality. Area loss as a result of patterning will also receive attention. Progress in these areas alone could yield an 8%, 30W module. For the record, critical tests need to be made to assess the effect of the new i-ZnO that is being used. The optimization of the ZnO will also be critically examined in terms of contact resistance and optical absorption. We hope also to examine the electrical/optical loss tradeoff for the new doped ZnO that is being used. We also have an idea for increasing the deposition rate for the doped ZnO. Work with hollow cathode sputtering as a means of depositing the window layer will be resumed. Module lamination processes will continue to be refined. We expect to start some outdoor life testing with large laminated CIGS modules. Additional modules will be shipped to NREL for performance verification.

If not in Q2, then certainly in Q3 we will set up to compare integrated energy production from CIGS, a-Si:H, and c-Si. At some point we will again fabricate a test a-Si:H/CIGS mechanically-stacked tandem module.

8) Other news

Approximately 75kW of the 112kW a-Si order from Germany has been shipped. Work is also under way on a-Si orders from Greece. All of the equipment has been installed in Tianjin and the factory is in the start-up phase. Equipment shipments to Heliodomi (Greece) are in progress. The number of personnel stands at about 50. Two articles have been submitted for a special issue of Solar Energy that will focus on thin film solar cells. One is a technical article about new technologies for CIGS, and the other a more general article about the commercialization of thin films. EPV will make two presentations at the 19th European PVSEC, one plenary, and one oral, the latter being on the hybrid CIGS process.

Sincerely,

Alan E. Delahoy Principal Investigator

Ala Z. - Delaloy

Leon Chen Senior Scientist